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BENZENE. ENVIRONMENTAL SOURCES OF CONTAMINATION, AMBIENT LEVELS, AND FATE

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Syracuse University Research Corporation

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BENZENE

ENVIRONMENTAL SOURCES OF CONTAMINATION, AMBIENT LEVELS, AND FATE

DECEMBER 1974

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This report reviews and evaluates available information pertinent to an assessment of benzene contamination of the environment. Benzene losses from commercial (production and use) and non-commercial (automotive emissions and oil spills) sources are considered. It is estimated that of the total quantity that is released to the environment more than half results from motor vehicle emissions. Monitoring data somewhat support this contention. Available information on the environmental persistence of benzene suggests that it degrades slowly.

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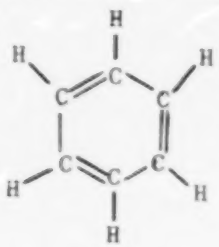
I. INTRODUCTION

This report reviews and evaluates available information that is pertinent to an assessment of benzene contamination of the environment. Physical and chemical properties, monitoring data, and environmental fate information are considered. In addition, the possible sources (both natural and man-made) of benzene in the environment are reviewed and quantitatively compared.

II. CHEMICAL STRUCTURE AND PROPERTIES

"Benzene, C_6H_6, is a volatile, colorless, and flammable liquid aromatic hydrocarbon, which possesses a very characteristic odor" (Ayers and Muder, 1964). The compound consists of a planar molecule with six carbon atoms formed into a hexagon. Several chemical structure representations of benzene have been suggested (e.g. the Kekule structures I and II), but the most frequently



Kekule Ring Formula
I

Abbreviated Kekule Formula
II

III

used formula, which gives a more realistic picture of the structure of benzene, is depicted by a hexagon with a circle in the middle (III). Each C-C and C-H bond in benzene is 1.39Å and 1.08Å long, respectively.

Benzene possesses greater thermal stability than would normally be predicted from the Kekule formula (3 double and 3 single C-C bonds). This difference (36.0 kcal/mole) between the energy required for dehydrogenation of cyclohexane

to benzene and the energy normally required for the formation of three double bonds is attributed to the resonance energy of benzene. The resonance energy is considered to be due to the interaction of the six π electrons which form "doughnut" shaped electron orbitals above and below the plane of the ring.

A number of physical properties of benzene are listed in Table 1. The water solubility (1800 ppm) and volatility (vapor pressure - 100 mm Hg at 26°C) are important parameters to environmental considerations. These parameters are temperature dependent and may be affected by various environmental conditions. For example, McAuliffe (1963) has reviewed a number

Table I. Properties of Benzene (Ayers & Muder, 1964)

Constant	Value
fp, °C	5.553
bp, °C	80.100
density, at 25°C, g/ml	0.8737
vapor pressure at 26.075°C, mm Hg	100
refractive index, n_D^{25}	1.49792
viscosity (absolute) at 20°C, cP	0.6468
surface tension at 25°C, dyn/cm	28.18
critical temp, °C	289.45
critical pressure, atm	48.6
critical density, g/ml	0.300
flash point (closed cup), °C	-11.1
ignition temp in air, °C	538
flammability limits in air, vol %	1.5-8.0
heat of fusion, kcal/mole	2.351
heat of vaporization at 80.100°C, kcal/mole	8.090
heat of combustion at constant pressure and 25°C (liquid C_6H_6 to liquid H_2O and gaseous CO_2), kcal/g	9.999
solubility in water at 25°C, g/100 g water	0.180
solubility of water in benzene at 25°C, g/100 g benzene	0.05

of reported values (1730-1790 ppm) for the solubility of benzene in water. The variation is probably attributable to different temperatures or the low precision of the techniques. Both salting-in and salting-out (increase and decrease in solubility) effects have been noted for benzene in aqueous solutions (Giacomelli and Spinetti, 1972). Sutton and Calder (1974) have noted a decrease in the solubility of higher molecular weight n-paraffins in salt water compared to distilled water. A similar decrease occurs with the water soluble fraction (including benzene) of crude oils (Lee et al., 1974). Thus the solubility of benzene in salt water is probably less than the reported distilled water value.

The benzene product available commercially is extremely pure. The specifications for the various commercial products are noted in Table II.

Table II. Physical Specifications of Commercial Benzene
(ASTM D835, 1973; ASTM D2359, 1974)

	Industrial Grade	Refined	Refined (Nitration Grade)
Distillation Range, 760 mm	Not more than 2°C including 80.1°C	Not more than 1°C including 80.1°C	Not more than 1°C including 80.1°C
Specific Gravity, 15.56/15/56°	0.875-0.886	0.8820-0.8860	0.8820-0.8860
Thiophene	--	1 ppm max	--
Nonaromatics	--	0.15 percent max	--

Gas chromatographic analysis has shown that no more than about 0.2% and usually no more than 0.1% hydrocarbon impurities (e.g. paraffinic, cycloparaffinic, olefinic hydrocarbons and toluene) are found in commercial benzene which has a boiling range no greater than 1°C. Other impurities in the commercial product include traces of thiophene and carbon disulfide (Ayers and Muder, 1964).

III. BENZENE CHEMISTRY

This section reviews chemical reactions which are commercially or environmentally important. Since the major commercial use of benzene is as a chemical intermediate, the number of commercial reactions is quite large.

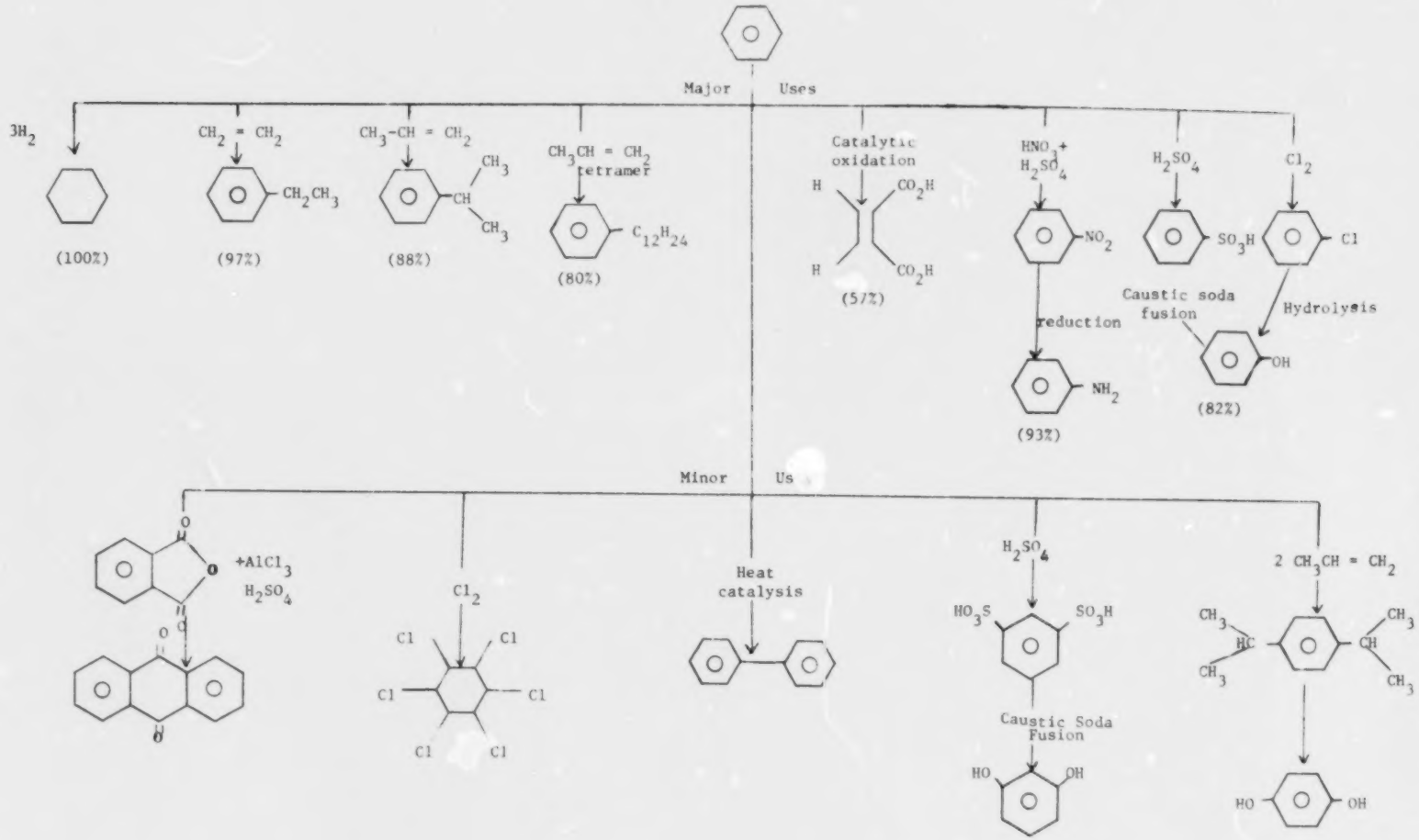
A. Reactions Involved in Uses.

Benzene is an important building block for a number of high volume chemicals including ethylbenzene (raw material for styrene), phenol, dodecylbenzene (raw material for surfactants), nitrobenzene (raw material for aniline), cyclohexane, chlorobenzene (raw material for DDT), dichlorobenzenes, and maleic anhydride. Table III depicts the commercial chemical reactions and the yields and conditions used to make the derivatives of benzene. In all cases, these reactions are carried out with catalysts, strong acids, or elevated temperatures and/or pressures and, therefore, are not likely environmental processes.

B. Hydrolysis

The benzene ring does not react with water or hydroxyl ions (OH^-) unless it is substituted with a sufficient number of powerful electronegative groups. For example, nitrobenzene reacts with strong sodium hydroxide to give o-nitrophenol (Ayers and Muder, 1964). Thus hydrolysis of benzene, which contains no electronegative substituents, is an extremely slow process which occurs only at elevated temperatures and pressures. For example, phenol has been formed

Table III Commercially Important Reactions of Benzene*
(Ayers and Muder, 1964; Erskine, 1972)



* Numbers in parenthesis indicate yields based on benzene starting material.

as a product of autoclave heating of benzene with 20% NaOH at 300-400°C with oxides of vanadium (Ayers and Muder, 1964). Commercially, benzene is hydrolyzed to phenol by first placing a good leaving group on the ring (e.g. - Cl).

C. Oxidation

Benzene can be oxidized to a number of different products, but usually catalysts and/or elevated temperatures and pressures are necessary. For instance, benzene is not affected by ordinary oxidizing agents (e.g., permanganate or chromic acid) until rigorous conditions are realized, in which case, complete oxidation to water and carbon oxides occurs. Commercially, benzene is catalytically oxidized to maleic anhydride and other by-products using air or oxygen at elevated temperatures with vanadium oxide catalyst. Both benzoquinone and phenol have been isolated from benzene that has been exposed to air and elevated temperatures (410-800°C) without catalysts.

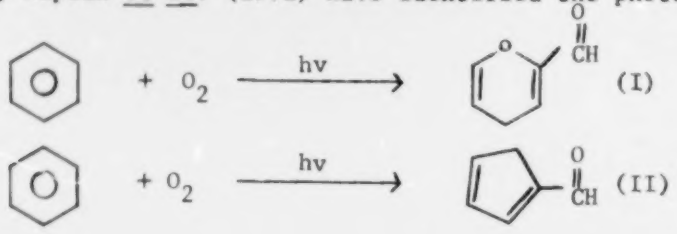
Boocock and Cvetanovic (1961) have studied the reaction of oxygen atoms, produced by mercury photosensitized decomposition of nitrous oxide, with benzene. They reported the formation of a "non-volatile material probably largely aldehydic in character" as well as smaller amounts of phenol and carbon monoxide.

Smith and Norman (1963) examined the oxidation of benzene and toluene with Fenton's reagent (Fe^{++} and H_2O_2). The suggested reactive species is the hydroxyl radical and the resulting products from benzene are phenol and biphenyl (dimerization).

D. Photochemistry

As can be seen in Figure 1, benzene does not absorb light directly in appreciable amounts at wavelengths longer than 280 nm (2800Å) when dissolved in cyclohexane. However, slight shifts in wavelength absorption might be expected in more representative environmental media (e.g., in water or adsorbed on particulate matter). For example, Chien (1965) measured the ultraviolet absorption spectra of liquid benzene under 1 atm. of oxygen (see Figure 2). In contrast, benzene vapor in air only absorbs light at 275 nm or less (Noyes et al., 1966). Since the ozone layer in the upper atmosphere effectively filters out wavelengths of light less than 290 nm, direct excitation of benzene in the environment is unlikely unless a substantial wavelength shift is caused by the media. However, in water or soil, indirect excitation may be possible due to the presence of sensitizers. Several investigators have studied the photolysis of benzene with <290 nm light and these studies will be briefly reviewed.

Benzene has been photolyzed with <290 nm light both in the vapor phase and in oxygenated aqueous solution. Luria and Stein (1970) exposed an oxygenated aqueous solution of benzene to 253.7 nm light and reported the formation of 2-formyl-4H-pyran (I). However, with convincing spectra data and synthesis, Kaplan et al. (1971) have identified the photoproduct as



cyclopentadiene-carboxaldehyde (II). Jackson and co-workers (1967) photolyzed benzene vapor (10 Torr) at 147 nm after the benzene was first degassed under vacuum. Gaseous products formed in the reaction included acetylene, ethylene,

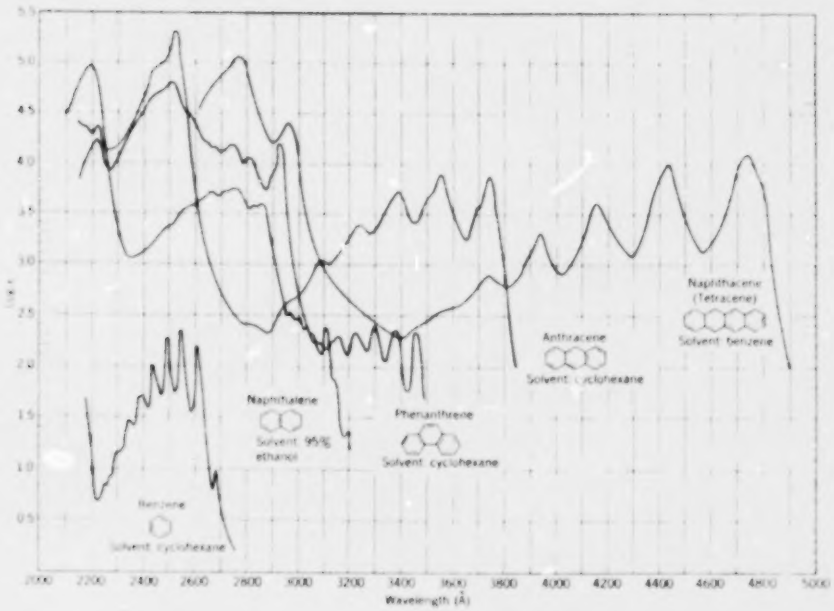


Figure 1. Electronic Absorption Spectra of Benzene, Naphthalene, Phenanthrene, Anthracene, and Naphthacene (Silverstein and Bassler, 1968, p. 166) Permission granted by John Wiley & Sons, Inc.

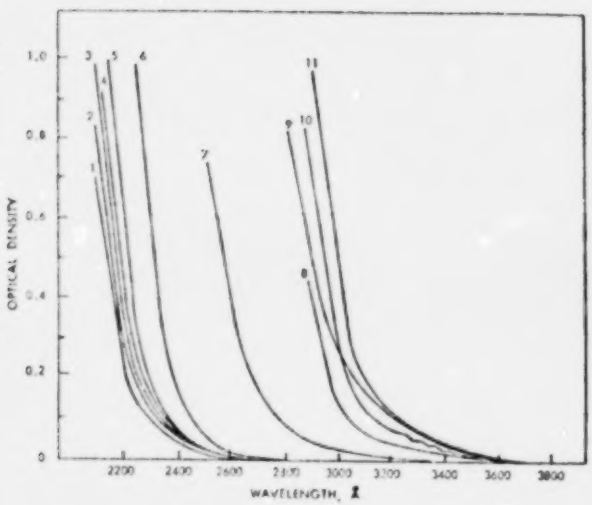


Figure 2. Ultraviolet absorption spectra (1-cm. path length, 1 atm. of oxygen) of: (1) 2,2-dimethylbutane; (2) 2-methylpentane; (3) 2,3-dimethylbutane; (4) n-heptane, 2,2,4-trimethylpentane (isooctane) and 2,4-dimethylpentane; (5) 2,3-dimethylpentane; (6) cyclohexane and methylcyclohexane; (7) octene-1; (8) chlorobenzene; (9) cyclohexene and cyclooctene; (10) benzene; (11) cuemen and toluene. (Chien, 1965). Reprinted with permission from J. Phys. Chem., 69, 12, 4317-25. Copyright by the American Chemical Society.

methylacetylene, vinylacetylene, and butene. However, the major product is a polymeric material. Irina and Kurien (1973) photolyzed benzene vapor in the presence of oxygen with 253.7 nm light. They isolated mucondialdehyde (HCOCH=CHCH=CHCHO) when organic solvents were used as trapping agents; phenol was isolated with water in the trap. Matsuura and Omura (1974) have reviewed several studies where atomic oxygen photochemically generated from various sources reacted with benzene to form phenol. Atomic oxygen is generated from the photodecomposition of nitrogen dioxide, which is frequently found in high concentrations in heavily polluted air (Altshuller and Bufalini, 1971).

Because benzene is frequently detected in heavily polluted air samples, it has been photolyzed under simulated smog conditions. Although reaction conditions have varied considerably from researcher to researcher (all use >290 nm light), benzene has been characterized as one of the least reactive hydrocarbons (in terms of hydrocarbon loss) along with acetylene and paraffinic hydrocarbons (Altshuller and Bufalini, 1971). However, some reaction does occur. Laity et al. (1973) reported that benzene disappeared in a steel photochemical smog chamber 30% slower than toluene. Similar results were reported by Stephens (1973). He irradiated an ambient air sample for 4 hours with both artificial and natural sunlight and found a decrease of benzene concentration to 7 ppb from an initial concentration of 8 ppb. Heuss and Glasson (1968) also found a low reactivity for benzene both in terms of eye irritation and rate of nitrogen dioxide formation (important step in the formation of photochemical smog). In most cases, these studies were run for a relatively short period of time (matter of hours) and, therefore, the long-term stability of benzene under atmospheric conditions is unknown. However, it has been demonstrated that under smog conditions, benzene is not completely inert.

IV. ENVIRONMENTAL EXPOSURE FACTORS AND MONITORING

A. Benzene Contamination from Commercial Sources

Benzene is produced in huge quantities in the United States. Over ten billion lbs. were produced in 1973 (U.S. Tariff Commission, 1974). In 1970, benzene was the second largest primary organic compound in terms of production and production value (ethylene first) (SRI, 1971). For the most part, benzene is used for synthesis of other raw materials for the commercial organic chemical industry (see Figure 3). Quantities of benzenes consumed in producing the major by-products for the period 1961-1971 are tabulated in Table IV.

The amount of benzene released to the environment during production, storage, transport, and raw material uses is unknown. However, some estimates can be suggested.

1. Production

Benzene can be derived from coal or petroleum, but the majority (88%) is now produced from petroleum sources. Only small amounts of benzene are present in crude oil so reforming is usually necessary. Three gallons of crude light oil (55-70% benzene) are generated for each ton of coal carbonized to coke and this light oil is the major source of coal benzene. Table V lists the benzene capacities, geographical location and name of the large commercial petroleum derived benzene producers as of January 1, 1972. Table VI presents the benzene capacity derived from coke production. Figure 4 depicts the geographic distribution of the production plants (Erskine, 1972). From the map in Figure 4, it can be seen that a few plants are located along the Mississippi River, but the vast majority are located along the Gulf of Mexico, especially along the Texas coast.

Benzene is usually stored in steel tanks and shipped in railroad tank cars, tank trucks, 55-gal. returnable and single-trip metal drums, and

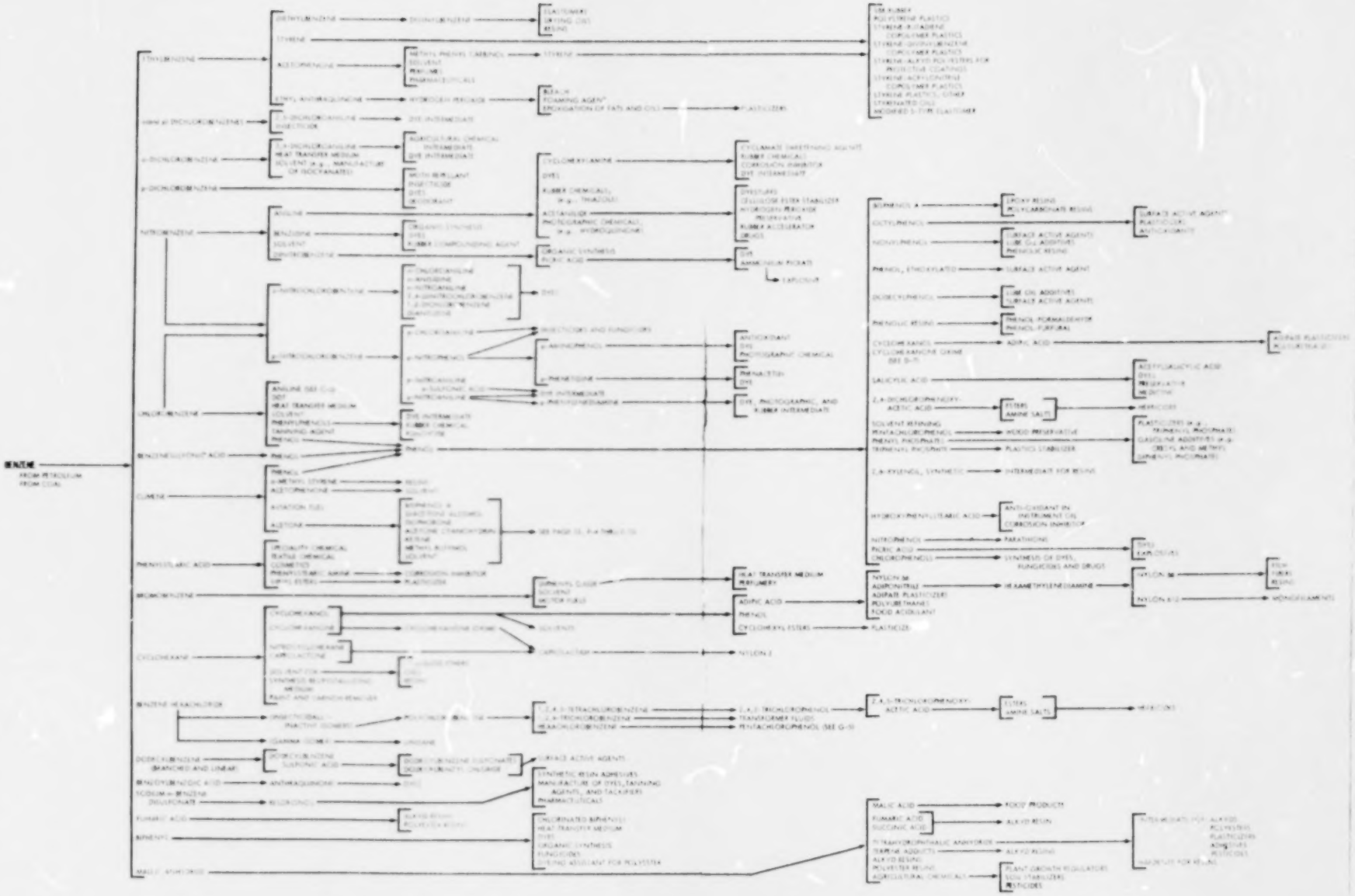


Figure 3 Commercial Uses of Benzene and Benzene Derivatives (Chemical Origins and Markets, Stanford Research Institute, 1967, pp. 18-19.)

Table IV. Benzene Consumption (millions of pounds)
(Erskine, 1972)

Year	Aniline	Cyclo-hexane	DDT	Detergent Alkylate	Dichloro-benzene	Ethyl-benzene	Maleic Anhydride	Phenol	Other Non-fuel Uses	Total
1961	110	404	125	195	70	1489	109	757	520	3780
1962	123	477	122	221	85	1587	110	795	299	3820
1963	139	604	131	202	87	1703	111	890	498	4365
1964	152	851	90	224	80	2057	155	1083	147	4843
1965	175	1162	103	250	67	2415	179	1207	375	5930
1966	214	1349	103	286	73	2653	237	1325	272	6511
1967	202	1332	76	273	73	2695	235	1345	331	6562
1968	236	1586	101	303	86	3066	254	1526	-15	7136
1969	299	1710	90	298	76	3894	281	1712	412	8775
1970	357	1363	43	317	85	3770	301	1803	544	8584
1971	297	1311	43	323	94	3709	325	1610	676	8385
% of Total (1971)	3.5	15.6	0.5	3.9	1.1	44.2	3.9	19.2	8.1	100

Table V Petroleum Based Benzene Production Plant Location and Capacity (Erskine, 1972)

Company	Location	Benzene Capacity (10^6 lbs.)
Allied Chemical	Winnie, Texas	37
Amerada Hess Corp.	St. Croix, Virgin Islands	169
American Petrofina, Inc.	Big Spring, Texas	220
Ashland Oil, Inc.	Ashland, Kentucky	441
	Tonawanda, New York	184
Atlantic Richfield Co.	Houston, Texas	323
	Wilmington, California	118
Atlantic Richfield-Union Oil	Nederland, Texas	132
Charter International Oil Co.	Houston, Texas	59
Cities Service Co., Inc.	Lake Charles, Louisiana	184
Coastal States Gas Prod. Co.	Corpus Christi, Texas	73
Commonwealth Oil Refining Co.	Penuelas, Puerto Rico	1176
Crown Central Petroleum Corp.	Houston, Texas	37
Dow Chemical Co.	Bay City, Michigan	220
	Freeport, Texas	294
Gulf Oil Corporation	Alliance, Louisiana	(514)
	Philadelphia, Pa.	242
	Port Arthur, Texas	279
Marathon Oil Co.	Detroit, Michigan	44
	Texas City, Texas	44
Mobil Oil Corp.	Beaumont, Texas	440
Monsanto Co.	Alvin, Texas	551
Pennzoil United, Inc.	Shreveport, Louisiana	88
Phillips Petrol. Co.	Sweeny, Texas	162
	Guayama, Puerto Rico	808
Shell Oil Co.	Deer Park, Texas	478
	Odessa, Texas	37
	Wilmington, California	147
	Wood River, Illinois	294
Skelly Oil Company	El Dorado, Kansas	88
Southwestern Oil & Ref. Co.	Corpus Christi, Texas	59
Standard Oil Co. of Calif.	El Segundo, Calif.	110
Standard Oil Co. (Ind.)	Texas City, Texas	625
Standard Oil Co. (N.J.)	Baton Rouge, Louisiana	441
	Baytown, Texas	441
Standard Oil Co. (Ohio)	Port Arthur, Texas	110
Sun Oil Co.	Marcus Hook, Pa.	110
	Corpus Christi, Texas	110
	Tulsa, Oklahoma	88
Tenneco, Inc.	Chalmette, Louisiana	110
Texaco, Inc.	Port Arthur, Texas	331
	Westville, N.J.	257
Union Carbide Corp.	Taft, Louisiana	367
Union Oil Co. of Calif.	Lemont, Ill.	220
Union Pacific Corp.	Corpus Christi, Texas	66
	Total Jan. 1, 1972	10,817
	Future Total	(11,332)

Table VI Coke-Oven Operators Producing Coal-Derived Benzene (Erskine, 1972)

Company	Location	Benzene Capacity January 1, 1972 (10^6 lbs.)
Armco Steel Corp.	Middletown, Ohio	18.4
	Houston, Texas	6.6
Bethlehem Steel Corp.	Bethlehem, Pa.	41.9
	Lackawanna, New York	55.1
	Sparrows Point, Maryland	110.2
C.F. & I. Steel Corp.	Pueblo, Col.	22.0
Interlake, Inc.	Toledo, Ohio	13.2
Ling-Temco-Vought, Inc.	Aliquippa, Pa.	73.5
Mead Corporation	Chattanooga, Tenn.	1.5
	Woodward, Ala.	10.3
Northwest Industries, Inc.	Lone Star, Texas	10.3
Republic Steel Corp.	Cleveland, Ohio	48.5
	Gladsden, Ala.	8.8
	Youngstown, Ohio	26.5
U.S. Steel Corp.	Clairton, Pa.	294.7
	Geneva, Utah	29.4
	Total	778.3

Figure 4 Geographical Location of Benzene Production Plants

· Derived from petroleum
* Derived from coal

barges. Because benzene is fairly volatile, it is likely that some release to the environment takes place during production, storage and transport. Although the quantity is unknown, it seems reasonable to assume that no more than 1% of the total production is lost in commercial production, storage and transport, especially because of the economic incentives to reduce losses. This loss would amount to approximately 80 million pounds in 1971 centered in relatively specific geographical areas.

2. Losses from Commercial Uses

As Figure 3 and Table IV demonstrate, the major commercial application of benzene is as a raw material for by-product synthesis. The efficiencies of these synthetic processes vary from approximately 100% yield (reduction of benzene to cyclohexane) to a low yield of 57% (oxidation of benzene to maleic anhydride) (Erskine, 1972). If one assumes that the difference between 100% yield and the reported yield (Erskine, 1972) is the amount of benzene potentially lost to the environment, the upper limit calculation in Table VII is possible. Of course these losses are much higher than is actually the case since some of the benzene is probably recycled or converted to a by-product and losses due to secondary synthetic steps are not excluded from the calculation. The "other non-fuel uses" include consumption for synthesis of anthraquinone, benzene hexachloride, chlorobenzene (other than for DDT, aniline, and phenol), diphenyl, nitrobenzene (other than for aniline), cumene (other than for phenol), and ethylbenzene (other than for styrene). Only extreme small amounts of benzene are used for solvent purposes. The quantity in this other non-fuel category is determined by difference (Erskine, 1972) and the losses vary depending upon the processes. Thus no loss calculation was made. However, this category only amounts to 8% of the total benzene consumption, at least in 1971 (in some years this figure is a minus number because it is determined by difference -- see Table IV).

Table VII Upper Limit of the Amount of Benzene Lost from By-Product Manufacturing Facilities (10^6 lbs.) in 1971

By-Product	Benzene Consumption	% of Total	100% minus % Yield *	Amount of Benzene Unaccounted for
Ethylbenzene	3709	44	3	111
Phenol	1610	19	18	290
Cyclohexane	1311	15	0	0
Maleic Anhydride	325	4	43	140
Detergent Alkylate	323	4	20	65
Aniline	297	3	7	21
Dichlorobenzene	94	1	15	14
DDT	43	1	40	17
Other Nonfuel Uses	676	8	--	--
				658

* The yields used are for overall yields to the various by-products. Some of these processes (e.g., phenol) are more than one step and, therefore, the losses may be not only benzene but also the intermediate compounds (e.g., chlorobenzene or cumene with phenol production).

As with production, the losses during synthesis of by-products are not evenly distributed geographically. Table VIII lists the major by-product producers along with the product manufactured, the capacity of the plants in terms of benzene required, and the geographical location. The latter is also depicted in Figure 5. The locations marked by an asterisk in Table IX indicate sites where the by-product producer also has a benzene production plant. In those instances where the by-product producer and benzene manufacturer are located in the same city, the possible losses due to transport are considerably lower. By comparing Figure 4 with Figure 5, it appears that the by-products are manufactured somewhat more in the northeast (closer to the market) while the benzene feed stock is produced closer to the source of petroleum. Thus, if large losses occur during transport, benzene contamination would occur somewhere between the southwest and the northeast, along the transportation routes. Lippian (1973) has considered collision losses when benzere is transported in tank cars (1.52 collisions/10^6 miles) but the quantity released in this fashion is unknown.

B. Benzene Contamination from Non-Commercial Sources

There are two important sources of benzene contamination which are not the result of commercial production and use of benzene: (1) oil spills, and (2) motor vehicle emissions. It has been estimated that the total oil influx into the ocean from routine discharges from tankers, accidents in port and on the high seas in exploration and production, in storage, in pipeline breaks, from spent lubricants, from incompletely burned fuels, and from untreated industrial and domestic sewage is between 11 - 12,000 million pounds per year (Blumer et al., 1971). The benzene content in crude oil varies from 0.001% to 0.4% (Green and Morrell, 1953). If an average percentage of 0.2% by weight of benzene in crude oil is assumed, a simple calculation suggests that between 22 - 24 million pounds of benzene is annually released into the environment with spilled oil.

Table VIII. By-Product Manufacturing Plants (Erskine, 1972)

Company	Location	Product (Benzene required 10^6 lbs.) Aniline	Cumene	Cyclohexane	Detergent Alkylate	Ethyl-benzene	Malwic Anhydride	Phenol
Allied Chem. Corp.	Moundsville, W.V.	35.9					27.9	
American Cyanamid Co.	Bound Brook, N.J. Willon Island, W.V.	53.8 358.6						
American Petrofina, Inc.	Big Spring, Texas*			46.7		68.1		
Ashland Oil, Inc.	Ashland, Kentucky*		222.67					
Baychem Corp.	New Martinsville, W.V.	89.7						
Clark Oil & Refining Co.	Blue Island, Ill.		74.2					
Coastal States Gas Prod. Co.	Corpus Christi, Texas*		103.9					
Continental Oil Co.	Baltimore, Maryland				79.4			
Cos-Mar, Inc.	Carville, Louisiana					503.4		
Dow Chemical Co.	Freeport, Texas* Midland, Mich.		7.42			567.7 264.9		236.6
E.I. DuPont de Nemours	Beaumont, Texas Gibbstown, N.J.	179.3 121.0						
El Paso Natural Gas Co.	Odessa, Texas					208.1		
First Mississippi Corp.	Pascagoula, Miss.	62.8						
Gulf Oil Corp.	Donaldsonville, Ga. Philadelphia, Pa.* Port Arthur, Texas*		259.8 334.0	200.6		427.7		
Koppers Co., Inc.	Bridgeville, Pa.						47.5	
Marathon Oil Company	Texas City, Texas*		155.9					
Monsanto Co.	Alvin, Texas* St. Louis, Missouri		475.0		89.3	1067.7	146.6	
Petro-Tex Chem. Corp.	Houston, Texas						69.8	
Phillips Petroleum Co	Sweeny, Texas * Guayana, P.R. *			200.6 331.3				

(continued)

Table VIII.(continued)

Reichhold Chemicals, Inc.	Elizabeth, N.J. Morris, Ill. Tuscaloosa, Ala.						41.9 83.8	151.0
Rubicon Chemicals, Inc.	Geismar, La.	46.6						
Shell & Common. Chem., Inc.	Penuelas, P.R.			181.9				
Shell Oil Co.	Deer Park, Texas * Torrance, Calif.		59.4			196.8		
Sinclair-Koppers Co.	Port Arthur, Texas					408.8		
Skelly Oil Co.	El Dorado, Kansas *		59.4					
Standard Oil Co. (Calif.)	El Segundo, Calif. * Richmond, Calif.		74.2		79.4			
Standard Oil Co. (Ind.)	Texas City, Texas *		37.1			681.3		
Standard Oil Co. (N.Y.)	Baytown, Texas *			242.7				
Standard Oil Co. (Ohio)	Port Arthur, Texas *				23.8			
Sun Oil Co.	Corpus Christi, Texas *		185.6			70.4		
Tenneco Inc.	Fords, N.J.						30.7	
Texaco Inc.	Port Arthur, Texas * Westville, N.J. *		103.9	242.7				
Union Carbide Corp.	Institute, W.V. Seadrift, Texas Ponce, P.R.		341.4		59.5 257.4			
Union Oil Co. of Calif.	Nederland, Texas			200.6				
Union Pacific Corp.	Corpus Christi, Texas *			84.0				
U.S. Steel Corp.	Neville Island, Pa.						55.9	
Witco Chem. Co., Inc.	Wilmington, Calif.				15.9			
Totals, January 1, 1972		445.6	1393.9	1731.1	347.2	5338.8	504.0	387.7

* Location where the by-product producer has a benzene production plant at the same site.

Figure 5. Geographical Location of Benzene By-Product Manufacturing Plants

Releases of benzene in motor vehicle emissions are somewhat more difficult to estimate. Both evaporation of the fuel and benzene emissions with the exhaust can be appreciable sources. In an urban environment, approximately 20% of the transportation hydrocarbon emissions (in terms of grams per vehicle mile for passenger vehicles) are due to evaporation, the rest coming from exhausts (Wendell et al., 1973). The total emissions of hydrocarbons from transportation sources is estimated to be 29,400 million pounds in 1971 (about 55% of the total hydrocarbon emission) (Council on Environment Quality, 1973). Benzene is found in varying amounts in gasoline (regular 1.35% by wt., premium 0.81%, API* fuel 0.12%; Sanders and Maynard, 1968). When the gasoline evaporates, the relative proportion of benzene may increase or decrease depending upon the volatility of all the gasoline components (benzene is one of the more volatile components of gasoline; Mair, 1964). However, if it is assumed that benzene is 1% of the gasoline vapors and gasoline vapors are 20% of the total annual motor vehicle emissions ($29,400 \times 10^6$ lbs. $\times$ .20 = $5,880 \times 10^6$ lbs.), the total annual (1971) emission of benzene from gasoline evaporation is 58.8 million pounds. Benzene consists of 2.15% by volume of the hydrocarbon emissions from a reciprocating engine (Schofield, 1974). On a weight basis, the percentage would amount to approximately 4%, since the lower molecular weight hydrocarbons (methane, acetylene, ethylene) make up more than 50% of the hydrocarbon emissions. Thus, the annual benzene emissions from motor vehicle exhausts would amount to approximately 940 million pounds in 1971. The total benzene motor vehicle emissions in 1971 would be approximately 1,000 million pounds and would be geographically distributed very similar to population.

*American Petroleum Institute

Table IX summarizes benzene emissions from both commercial production and use and non-production sources. These sources are probably the major sources, but other sources may be significant. For example, the other 45% of the hydrocarbon emission from non-transportation sources may contain considerable amounts of benzene, especially fossil fuel combustion processes (e.g., power plant). The quantities involved are unknown.

Table IX Comparisons of Benzene Emissions for 1971

Source	Geographic Location	Quantity (10^6 lbs.)
Commercial benzene production, storage and transport	Mostly the Southwest	~80 (assumed 1% of total production)
Commercial benzene use	Southwest and Northeast	658 (upper limit based on reaction yields)
Oil Spills	Oceans and Rivers	22-24
Motor Vehicle Emissions	Similar to Population Distribution	1,000

C. Environmental Monitoring and Analysis

1. Analysis Techniques

Techiques for determining benzene in air, water and blood have been reported. Usually some type of preconcentration step is required when measuring low concentrations, but a number of researchers have used direct analysis. For example, Bradley and coworkers (Bradley and Franzel, 1970; Bradley et al., 1972) used laser Raman spectroscopy for detection and identification of benzene down to approximately 20 ppm in water. The technique has

the advantage of no sample work-up and it can be used in the field. However, because of its low sensitivity, application is probably limited to monitoring high concentration effluents.

Harris et al. (1974) have investigated the potential for a direct, aqueous injection technique using combined gas chromatography-mass spectrometry (GC-MS). Although benzene was not one of the compounds examined, the technique is generally good to between 1-50 mg/ℓ (ppm) of water, which is not sufficient for relatively clean water.

Bramer et al. (1966) devised a continuous flow instrument for determining relative amounts of trace organics in chemical plant effluents based upon the ultraviolet (UV) absorption of the aqueous solution. A mercury discharge lamp (mostly 253.7 nm) was used as the light source. The method was sensitive to 50 ppb benzene, but since many other compounds besides benzene absorb UV light, the method is not specific for benzene.

In order to study animals subjected to 5000 ppm benzene, Fati (1969) used a technique which required the injection of 1 μℓ of blood directly into a gas chromatograph. Concentrations of 0.03 mg/1000 ml (ppm) of blood could be detected.

Direct analysis of air samples has also been used by Altshuller and coworkers (Altshuller and Clemons, 1962; Altshuller and Bellar, 1963). They used a direct injection (3 ml air sample) technique with gas chromatography to analyze benzene in ambient air samples and in synthetic photochemical "smogs". The flame ionization (FI) detector used with the gas chromatograph was sensitive enough for detection of individual aromatic hydrocarbons in the 0.05 - 1 ppm range in synthetic smogs (Altshuller and Clemons, 1962) and in the 0.005 to 4 ppm range in ambient air samples (Altshuller and Bellar, 1963).

Preconcentration or extraction techniques used for detecting low concentrations of benzene in air or water samples have varied considerably as is noted in Table X. Both liquids and solids have been used as adsorbents for concentrating the sample. The increased sensitivity derived from this approach is accompanied by greater work-up and handling times. Since handling of the sample increases the potential for losses, Wasik and Tsang (1970) have suggested the addition of predeuterated benzene before processing of the sample. By measuring the deuterated to undeuterated ratio after concentration, an accurate concentration of benzene in the sample can be determined. This technique has not been used in any of the preconcentration techniques.

For water samples, the most sensitive technique for benzene is the inert gas stripping method of Novak et al. (1973). In fact, the method was so sensitive that benzene and chloroform were found in relatively pure drinking water (benzene ~10^{-4} mg/ℓ). The authors suspect, and have some proof that the compounds are adsorbed from the laboratory atmosphere (chloroform is adsorbed from the laboratory atmosphere to concentrations of several ppm in water within 1 hr.) (Novak et al., 1973). This emphasizes the need for careful handling of the sample during manipulation in order to prevent contamination. The carbon-chloroform extract procedure used by Gordon and Goodley (1971), U.S. EPA (1972), and Friloux (1971) is a common procedure for isolating enough material for qualitative determinations. However, the procedure provides only approximate quantitative information because the adsorption and desorption efficiencies are usually not determined. For quantitative information, the efficiencies of adsorption on the carbon, losses during drying of the carbon, efficiency of the chloroform extraction, and losses during solvent reduction would have to be determined.

Both silica gel and activated charcoal have been used as room temperature adsorbents of benzene in air samples. With silica gel, a prefilter of molecular sieves is commonly used to remove the water vapor. Whitman and

Table X. Preconcentration Techniques for Analysis of Benzene in Air and Water Samples

Reference	Type of Sample	Adsorbent	Solvent	Qualitative and Quantitative Technique*	Limits of Detection
Zarrella et al. (1967)	Subsurface brines	--	Isooctane extraction Aqueous injection	U.V. absorption G.C.	~0.01 ppm ~0.01 ppm
Novak et al. (1973)	Water	-- Inert gas stripping	Organic solvent extr.	G.C. G.C.-FI, G.C.-MS	0.1 mg/l 0.1 ppb
Gordon and Goodley (1971)	Water	Carbon filter	Diethyl ether, chloroform, hexane extr. Chloroform or alcohol	G.C. G.C.-MS	
U.S. EPA (1972) Frilloux (1971)	Drinking water	Activated carbon	Chloroform	preparat. G.C., then IR; G.C.-MS	ppm-ppb range (not quantitative)
U.S. EPA (1974)	Drinking water (New Orleans)	Activated carbon XAD resin Liquid-Liquid extr. Inert gas stripping (trap on G.C. column)	Chloroform Ethyl ether Tetralin	G.C., G.C.-MS G.C., G.C.-MS Direct inject. into G.C., G.C.-MS	ppb range
Dambrauskas and Cook (1963)	Air	Methanol (with dry ice)	Methanol	UV	accuracy below 10 ppm "poor"
Benoze (1965)	Air	Silica gel	n-Heptane	U.V. (not specific)	
Whitman and Johnston (1964)	Air	Silica gel molecular sieve prefilter	iso-Propyl benzene	G.C.	detected 7-8 mg/m^3
Sherwood (1971)	Air	Silica gel (personal air sampler)	Ethanol	G.C.	ppm range
Elkins et al. (1962)	Air	Silica gel	iso-Propyl alcohol and several other solvents	U.V. (not specific)	2-40 ppm
Kolbovsky (1969)	Air	Silica gel	--	Indicator tube (cerium sulphate) - not specific	sensitivity-0.005 mg/l accuracy ±15%
Cooper et al. (1974)	Air	Charcoal	Organic solvent	G.C., G.C.-MS	20 ppm (10l sample)
Ash and Lynch (1971)	Air	Charcoal	Carbon disulfide	G.C.-FI	30 ppm
White et al. (1970)	Air	Charcoal	Carbon disulfide	G.C.-FI	used down to 12 ppm
Grob and Grob (1971)	Air	Charcoal	Carbon disulfide	G.C.-MS	50 ppb
Seligan et al. (1965)	Air	Firebrick (cold trap)	--	rapid heating into G.C.-FI	1 ppb ± 25%
Lonneman et al. (1968)	Air	Glass bead (cold trap)	--	rapid heating into G.C.-FI	1 ppb
Williams (1965)	Air	G.C. packing (cold trap)	--	rapid heating into G.C.-EC, G.C.-FI	<10 ppb
Solecky et al. (1967)	Air	G.C. packing (cold trap)	--	rapid heating into G.C.-FI	
Pilar and Graydon (1973)	Air	G.C. packing (cold trap)	--	rapid heating into G.C.-FI	14.3 ± 2.5 ppb
Stephens (1973)	Air	G.C. packing (cold trap)	--	rapid heating into G.C.-FI	0.1-0.2 ppb (100 ml sample)

*Ultraviolet spectrometry (U.V.); gas chromatography (G.C.); flame ionization detector (FI); electron capture detector (EC); mass spectrometry (MS).

Johnston (1964) have demonstrated that water vapor can have a drastic effect on benzene adsorption on silica gel. This problem is eliminated when activated charcoal adsorbent is used since the affinity of water for activated charcoal (or carbon) is very low. Thus, in moist atmospheres, activated charcoal has been recommended for sampling compounds that are weakly adsorbed on silica gel (Buchwald, 1965).

Cold trap concentration of benzene from air samples followed by direct injection into a gas chromatograph appears to be the most sensitive technique. However, the procedure has the disadvantage that the analyst has only one sample with which to work. In contrast, the charcoal or silica gel adsorption procedure followed by solvent extract provides the analyst an opportunity to store the sample and to inject numerous aliquots into the gas chromatograph.

2. Monitoring Data

The available ambient monitoring data for benzene are summarized in Table XI. The information provides some suggestive evidence (but not proof) of the environmental contamination sources of benzene. For example, the EPA analytical study of finished waters (US EPA, 1972) drawn from the Mississippi River also examined the organic waste effluents from sixty industries which are discharging into the Mississippi. Fifty-three organic chemicals ranging from acetone to toluene were identified in eleven plants. Benzene was not detected thus suggesting a contamination source other than industrial water effluents.

Pilar and Graydon (1973) studied the concentration of benzene and toluene at seventeen sampling stations and took samples continuously at one-hour intervals for nine days. Based upon (1) the ratio of toluene to benzene, (2) the distinct maxima for both toluene and benzene at 0700, 1500 and 2100 hrs., and (3) the relative concentrations at various sampling stations, the authors concluded that there was little doubt that the benzene contamination was linked to automotive transportation. The toluene-benzene ratio found in

Table XI Ambient Monitoring Data for Benzene

Reference	Type of Sample	Geographical Location	Sampling* Method Used	Analysis* Technique	Quantities Detected
Gordon and Goodley (1971)	Water and mud	Lower Tennessee River	CCE liquid-liquid extract	GC-MS	Not reported
U.S. EPA (1972)	Finished water	Carrollton Plant, New Orleans	CCE	Preparative GC,	Not attempted
Friloux (1971)	Finished water	U.S. PHS Hospital Carville, La.			"trace" ppb-ppm range
Novak et al. (1973)	"Polluted" and "pure" drinking water	Prague, Czechoslovakia	Inert gas stripping	GC, GC-MS	~0.1 ppb
Williams (1965)	Ambient air	Vancouver, Canada	Cold trap - GC column	rapid heating into GC	1-10 ppb
Smoyer et al. (1971)	Ambient air	Vicinity of solvent reclamation plant	Grab sample	direct injection into GC; MS, IR	23 ppm
Neligan et al. (1965)	Ambient air	Los Angeles basin	Cold trap - firebrick	rapid heating into GC	.005-.022 ppm (V/V)
Altshuller and Bellar (1963)	Ambient air	Downtown Los Angeles	Grab sample	direct injection into GC	0.015-0.06 ppm (V/V)
Lonneman et al. (1968)	Ambient air	Los Angeles basin	Cold trap - glass beads	rapid heating into GC	aver. 0.015 ppm highest 0.057 ppm (V/V)
Grob and Grob (1971)	Ambient air	Zurich, Switzerland	Charcoal trap - carbon disulfide extract	GC-MS GC-FI	0.054 ppm
Stephens (1973)	Ambient air	Riverside, California	Cold trap - GC column	CC-FI	0.007-0.008 ppm
Pilar and Graydon (1973)	Ambient air	Toronto, Canada	Cold trap - GC column	GC-FI	aver. 0.013 ppm; highest 0.098 ppm

*CCE - carbon chloroform extract; GC - gas chromatography; FI - flame ionization; IR - infrared spectrometry; MS - mass spectrometry.

Toronto air was higher than in automotive exhaust. This high ratio in ambient air has also been noted by Lonneman et al. (1968). Several possible explanations were suggested by Pilar and Graydon (1973) including (1) the fact that gasoline vapors have a relatively high toluene-benzene ratio suggesting the possibility of direct evaporation as a source, (2) inapplicable automotive exhaust monitoring data for the Toronto situation, and (3) physical or chemical changes between emission and air sampling.

V. ENVIRONMENTAL FATE

A. Degradation or Alteration Processes

1. Biological Transformation of Benzene

a. Microbial Degradation

While the microbial degradation of benzene has been the subject of much recent research and review, attention has focused primarily on the enzymatic mechanisms of degradation and their relationship to mammalian systems (e.g., Smith and Rosazza, 1974) rather than on an evaluation of biodegradation under conditions approximating environmental exposure. Nonetheless, the information that is available indicates that benzene is susceptible to attack by a variety of microorganisms utilizing pathways analogous to those of a number of aromatic compounds. While such degradation probably occurs under certain environmental conditions, the rates of degradation in the natural environment cannot be extrapolated from the available data.

(i) Degradation by Mixed Cultures of Microorganisms

The effect of mixed microbial cultures on benzene has been studied primarily to determine if benzene can or will be degraded under waste treatment plant conditions. These studies indicate that benzene can be degraded but that the rates of such degradation vary considerably depending upon the incubation period and previous acclimation of the microorganisms. The results of these experiments are given in Table XII.

Table XII: Degradation of Benzene by Mixed Cultures of Microorganisms

Reference	Source of Microorganisms	Adaptation	Incubation Time	Benzene conc. [Activated sludge conc.]	Oxygen Consumed
Bogan and Sawyer (1955)	Activated sludge	none	5 days (standard dilution BOD technique)		1.9% of theoretical
	Domestic sewage	14 days (10 ppm up to 100 ppm then 48 hrs. with no exposure to test compound)	5 days (standard dilution BOD technique)		2.4% of theoretical
			6 hr (Warburg)	50-100 ppm [~3000 ppm]	3.3% of theoretical
Marion and Malaney (1963)	Activated sludge	none	24 hr (Warburg)	500 mg/l [2500 mg/l]	about equal to endogenous control
			160 hr (Warburg)	500 mg/l [2500 mg/l]	1.1-1.3 times endogenous control
Malaney (1960)	Activated sludge	aniline as sole carbon source (20 day feeding program)	190 hr (Warburg)	500 mg/l [2500 mg/l]	2 times endogenous control
Chambers et al. (1963)	Soil, compost, or mud from a petroleum plant waste lagoon (predominantly *Pseudomonas*)	phenol as sole carbon source	28 hr (Warburg)	100 mg/l	1.6 times endogenous control 0.2 times phenol control (90 min.)

Interpretation of the results obtained is very difficult. The sludge used by Marion and Malaney (1963) was not washed before placement in the Warburg flask and, therefore, the carbon sources in the sludge were available to the microorganisms. In several of the 24 hr test runs, the oxygen uptake measured with benzene was less than the control, suggesting inhibition. In the longer runs, only a slight difference was noted between the control and benzene. The results of Bogan and Sawyer (1955) have the endogenous rate subtracted from the reported oxygen consumption. Again only a small increase in oxygen consumption is noted and, of the five hydrocarbons studied, only t-butylbenzene was more resistant to biochemical oxidation. Chambers et al. (1963) concluded that with their phenol adapted seed, the "benzenes were oxidized with difficulty or not at all." In fact, the benzene rate was similar to such compounds as 1,3,5-trichlorobenzene and 1,3,5-trinitrobenzene which one would expect to be fairly persistent. Perhaps the safest conclusion from the four studies in Table XII is that benzene may be biodegradable, but at a very slow rate.

In a study of the biodegradability of chlorinated analogs of hydrocarbons, Okey and Bogan (1965) developed an adapted sludge that was capable of growing on benzene as the sole source of carbon (50 mg/ℓ). The sludge utilized about 45% of the total substrate (benzene) COD in 10 hours.

Thus, it has been demonstrated that benzene can serve as a carbon and energy source for a culture enriched on benzene and derived from a treatment plant activated sludge.

Biodegradation of hydrocarbons in marine water relative to fresh water is seriously limited by the scarcity of nitrogen and phosphorus (Atlas and Bartha, 1973). Since benzene is a component of crude oil, understanding its fate in marine waters, where most large oil spills take place, is very important. Unfortunately, no mixed culture studies with benzene in sea water have been attempted. However, with fifteen microorganisms isolated from sea water or sediment, Bartha (1970) only found one organism (Brevibacterium) capable of utilizing benzene for growth. In a similar study by Perry and Cerniglia (1973), where a large number of microorganisms were isolated and the number of organisms capable of growth on the substrate was used as criteria for biodegradability, the aromatics, in general, were found to be more recalcitrant than any other hydrocarbon except for cycloalkanes. An assessment of benzene degradation under marine conditions should consider the results of Walsh and Mitchell (1973). These authors showed that 0.1 ppm benzene inhibits chemotaxis (chemical communication resulting in attraction of a microorganism to a test substrate) by 50% in a motile marine Pseudomonas. The importance of the effect is unknown since the concentration of 0.1 ppm is considerably higher than

what would be expected in marine waters, but the inhibition may have immediate effects on the rate of degradation or long-term effects on the diversity and population of marine organisms.

(ii) Degradation by Pure Cultures of Microorganisms

From the studies listed in Table XIII, it can be concluded that benzene can be degraded by a number of microorganisms. In some instances, the organism can use benzene as a carbon and energy source. However, pure culture studies provide very little degradation rate information because they are considerably removed from conditions experienced in nature. Rarely is the test substrate (benzene) the only source of carbon. Competition between different microorganisms for the available nutrients is ignored in pure cultures. The concentration of the test substrate is considerably higher than would occur in nature thus questioning whether the necessary enzymes that are induced at the high test concentrations would ever be induced under natural conditions. The work by Cofone et al. (1973) suggests that the induction period with Cladosporium resinae is slow (22 days) even at high concentrations (10 ml benzene overlayed on 100 ml of sterile salts solution). Nevertheless, the pure culture studies, combined with information obtained with cell-free extracts, do provide a great deal of information about the pathways of benzene degradation by microorganisms.

XIII. Pure Cultures of Microorganisms Which Degrade Benzene

Reference	Organism	Source	Incubation Period	Prior Acclimation	Metabolites Identified or Proposed
Cofone et al., 1973	Cladosporium resinae	Jet Fuel	34 days	-	-
Smith and Kosaric, 1974	Penicillium chrysogenum	Culture Collection*	1-3 days+	24 hrs on fresh soybean meal-glycose medium	Phenol and two unknown phenols
"	Cunninghamella blakesleeana	" "	"	"	"
"	Gliocladium deliquescens	" "	"	"	"
"	Streptomyces sp.	" "	"	"	"
"	Cunninghamella bainieri	" "	"	"	"
Bartha, 1970	Brevibacterium (K)	Sea water and sediments	not specified	-	-
Höfgn and Jaenicke, 1972	Moraxella B	River mud (by enrichment culture technique with benzene)	60 min.	-	cis-1,2-Dihydroxy-1,2-dihydrobenzene Catechol
Gibson et al., 1968	Pseudomonas putida	Soil (by enrichment culture technique with toluene)	40 min.	-	cis-1,2-Dihydroxy-1,2-dihydrobenzene Catechol
Gibson et al., 1970	Pseudomonas putida 39/D (mutant strain)	"	30 hrs.	-	cis-1,2-Dihydroxy-1,2-dihydrobenzene
Claus and Walker, 1964	Achromobacter sp.	"	150 min.	-	-
"	Pseudomonas sp.	"	150 min.	-	-
Marr and Stone, 1961	Mycobacterium rhodochrous	Soil (by enrichment culture technique with benzene)	120 min.	-	Catechol
"	Pseudomonas aeruginosa	"	120 min.	-	"

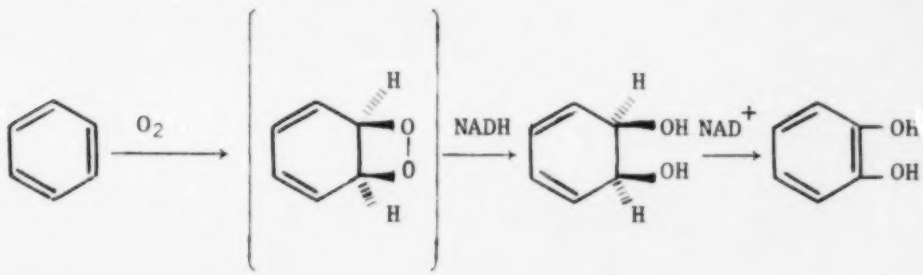
* benzene not used as sole source of carbon

+ selected for known ability to metabolize aromatic compounds

(iii) Pathways of Microbial Breakdown of Benzene

(a) Ring Attack

The primary step in the degradation of benzene by most bacteria seems to involve a dioxygenase enzyme leading to the formation of catechol via cis-1,2-dihydroxy-1,2-dihydrobenzene. Such a scheme is outlined in Figure 6.



Benzene — Hypothetical Dioxetane — cis - 1,2-Dihydroxy-1,2-dihydrobenzene — Catechol

Figure 6: Microbial Degradation of Benzene to Catechol (modified from Gibson, 1971; Högn and Jaenicke, 1972) Courtesy of Springer-Verlag.

Such a pattern is indicated by the results of Gibson and coworkers (1968, 1970) and Högn and Jaenicke (1972). Using $^{18}O_2$, Gibson et al. (1970) showed that both oxygen atoms added to benzene are derived from atmospheric oxygen. In addition to dioxygenase modification, evidence by Smith and Rosazza (1974) seems to indicate that monooxygenase systems also operate in certain microbial systems, resulting in the hydroxylation of benzene to phenol. Although phenol has long been proposed as an intermediate in the oxidation of benzene by some microorganisms (Kleinzeller and

Fencl, 1952), phenol has only recently been isolated from cultures grown in the presence of benzene (Smith and Rosazza, 1974).

(b) Ring Cleavage

Although a number of microorganisms have the ability to modify benzene, no organism is able to cleave the unsubstituted benzene ring directly. Instead, cleavage occurs with the metabolism of catechol which can be derived from benzene either by dioxygenase dihydroxylation or by the further hydroxylation of phenol. Bacterial ring cleavage of catechol may proceed by either ortho or meta fisshion as illustrated in Figure 7.

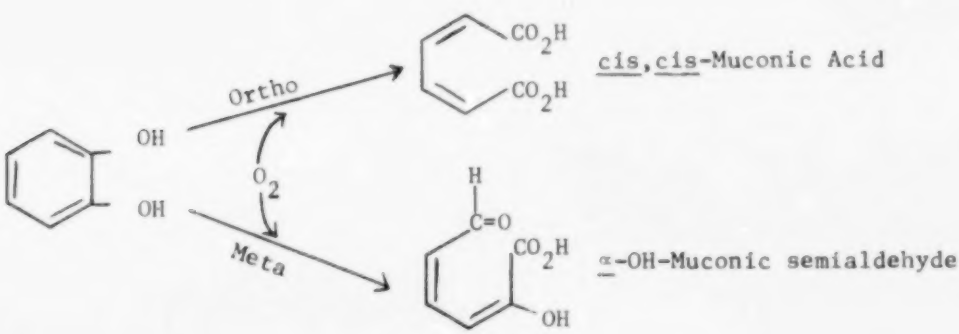


Figure 7: Ortho Fission of Catechol by Pseudomonas putida and Moraxella lwoffii and Meta Fission of Catechol by a Pseudomonas sp. (adapted from Chapman, 1972).

Both types of cleavage involve the addition of molecular oxygen through a non-heme ion dioxygenase (Dagley, 1972). With ortho cleavage, catechol is converted

to β-ketoadipic acid, whereas meta cleavage has been shown to result in the formation of acetaldehyde and pyruvic acid (Chapman, 1972). The details of these pathways are illustrated in Figure 8.

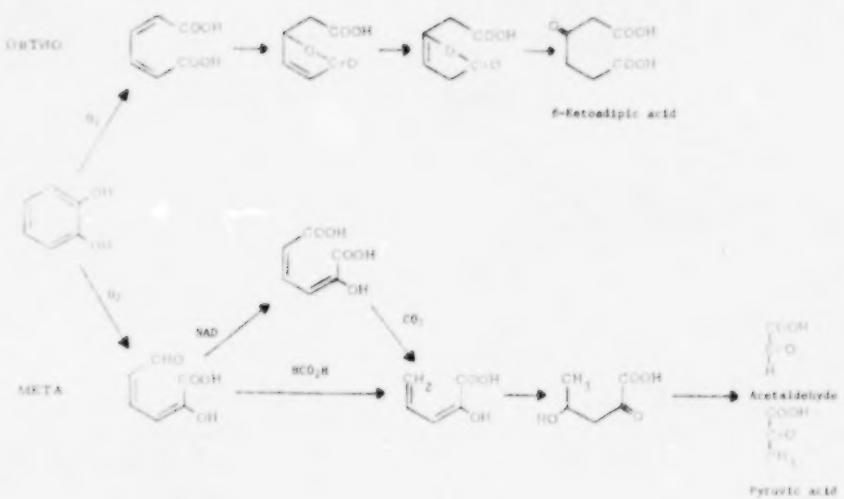


Figure 8: Benzene Ortho Fission Pathways by Pseudomonas putida and Moraxella lwoffii and Meta Fission by a Pseudomonas sp. (adapted from Chapman, 1972).

(b) Mammalian Metabolic Pathways

Since the initial demonstration of benzene conversion to phenol by mammals (Schultzen and Naunyn, 1867), a number of studies have been conducted in an attempt to delineate the pathways involved in the mammalian metabolism of benzene and related aromatic compounds. With the information available on the metabolism of benzene by rats and

rabbits, Gibson (1971) described the pathways of mammalian benzene metabolism illustrated in Figure 9. Although benzene oxide has not yet been conclusively demonstrated as a benzene intermediate and the formation of trans,-trans-muconic acid from catechol is still not completely understood, the metabolic scheme as presented does seem to account for what is currently known about the fate of benzene in mammals.

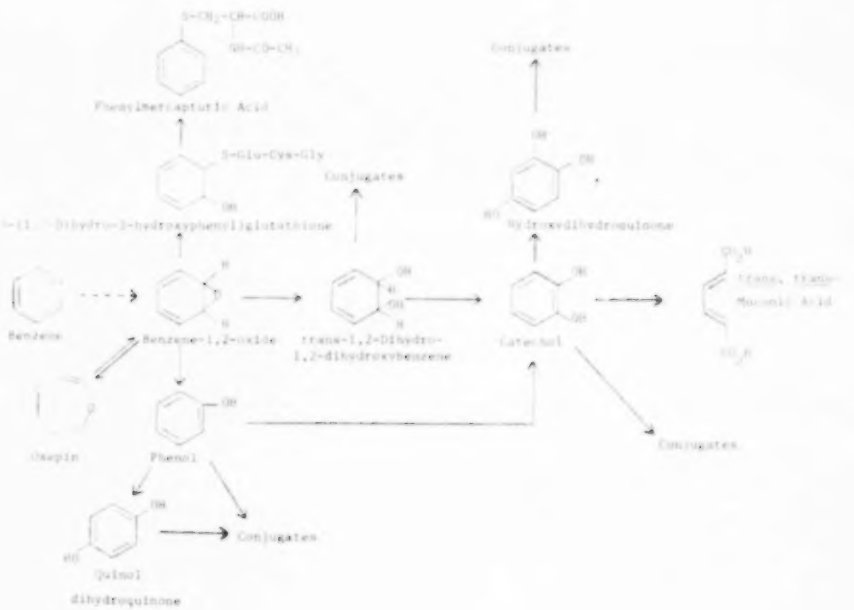


Figure 9: Proposed Pathways of Mammalian Benzene Metabolism Based on Studies with Rats and Rabbits (Adapted from Gibson, 1971) Courtesy of CRC Press.

(1) In Vivo Studies

Most of the general pathways presented in Figure 9 were proposed on the basis of early in vivo studies using rabbits. Porteous and Williams (1949a) administered

benzene orally to rabbits at a dose of 500 mg/kg. On analyzing urine samples, about twenty percent of the dosage was accounted for as conjugates of phenol, catechol, dihydroquinone, and hydroxydihydroquinone, with phenol conjugates comprising about half of the total conjugates recovered. In addition, small amounts of free phenol and muconic acid were also detected. On the basis of this study and experiments using related aromatic compounds, Garton and Williams (1949) postulated the following pattern of benzene metabolism:

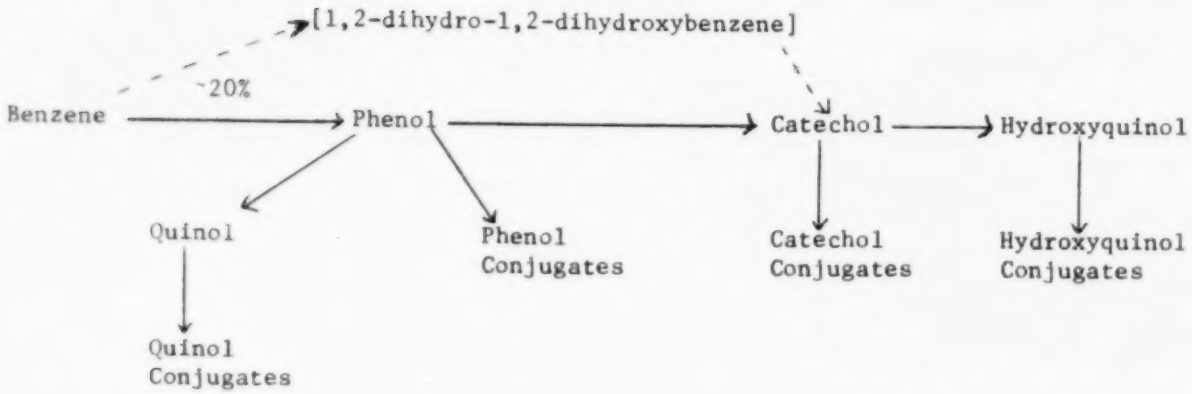


Figure 10: Primary Metabolic Pathways of Benzene in Rabbits as Proposed by Garton and Williams (1949).

In addition to the pathways identified through the analysis of metabolites indicated by solid lines in Figure 10, Porteous and Williams (1949b) proposed an alternate pathway for the formation of catechol involving 1,2-dihydro-1,2-dihydroxybenzene. This supposition was based on a comparison

of dihydroquinone:catechol ratios which were 1:1 with benzene and 10:1 with phenol as the substrate. The high ratio with phenol metabolism identified dihydroquinone as the primary metabolite, since it would be expected that the ratio would not change if phenol were the sole intermediate in the production of catechol from benzene (Porteous and Williams, 1949b). Parke and Williams (1953a and b) attempted to pursue this hypothesis with more quantitative analysis of ^{14}C-benzene. However, because they were unable to synthesize trans-1,2-dihydro-1,2-dihydroxybenzene and did not detect muconic acid in phenol fed rats, they erroneously suggested that the benzenediol was the sole precursor of muconic acid (Parke and Williams, 1953b).

With oral administration of benzene to rabbits at doses of 500 mg/kg, Parke and Williams (1951) demonstrated that muconic acid excreted in the urine was the trans,trans isomer and not the cis,cis form which might be expected on the basis of stereochemical considerations and which is found in microbial ortho cleavage (see Figure 7). The trans,trans isomer formation was subsequently confirmed in studies using radiolabelled benzene (Parke and Williams, 1953a). The details of formation of trans,trans-muconic acid are still not understood (Gibson, 1971).

Parke and Williams (1953a) also proposed phenylmercapturic acid as a minor metabolite (0.4-0.7% of dose) of benzene in rabbits. In rats administered benzene (1000 mg/kg) by stomach tube, a precursor of phenylmercapturic acid, which converted to phenylmercapturic acid on treatment with 1.5μℓ HCl, was identified in the mice (Knight and Young, 1958). A similar mercapturic acid precursor identified as N-acetyl-S-(1,2-dihydro-2-hydroxyphenol) cysteine was found in the urine of rabbits given intraperitoneal doses of 0.5 ml benzene (Sato et al., 1963). A more significant aspect of the study by Sato and coworkers (1963) was the tentative identification of 1,2-dihydro-1,2-dihydroxybenzene and its glucuronide by chromatographic and electrophoritic methods in the rabbit urine. The presence of both metabolites led the investigators to suggest that the epoxide may be a common intermediate.

(2) In Vitro Studies

Investigations of the in vitro metabolism of benzene have focused primarily on characterizing some of the individual reactions shown in Figure 9. The conversion of benzene to phenol has been the most extensively studied and is often used as an index of benzene metabolism. Phenol was identified as a metabolite of benzene in rat liver microsomes by both Daly and coworkers (1968) and Booth and Boyland (1957) after incubation periods of thirty to sixty minutes. In a similar study using both rabbit and rat liver

preparations, the metabolism of benzene to phenol and phenol conjugates was shown to be enhanced by pretreatment with benzene. This stimulation of benzene metabolism involved increased amino acid incorporation into microsomal protein and was suggestive of enzyme induction (Snyder *et al.*, 1967). Recently, Gonasum and coworkers (1973) have implicated a mixed function oxidase and the binding of benzene to cytochrome P-450 in the metabolism of benzene to phenol by mouse liver microsomes.

The *in vitro* metabolism of trans-1,2-dihydro-1,2-dihydroxybenzene has been studied by Ayengar and coworkers (1959) using a partially purified enzyme from rabbit liver. After incubation for thirty minutes, catechol was identified as the sole metabolic product which is consistent with Figure 9. The enzyme involved was named diol-dehydrogenase and the oxidation to catechol was coupled to the reduction of nicotinamide-adenine dinucleotide phosphate.

A major advance in the understanding of benzene metabolism was the synthesis of benzene oxide and its subsequent use in *in vitro* metabolism by Jerina and coworkers (1968). In this study, rabbit liver microsomes and the soluble fraction were incubated with benzene oxide for thirty to sixty minutes. The results of this work are summarized in Figure 11.

Figure 11: The In Vitro Metabolism of Benzene Oxide Using Rabbit Liver Microsomes and Soluble Fraction (adapted from Jerina et al., 1968)

Although the metabolites of benzene oxide coincide with those of benzene and thus implicate benzene oxide as an intermediate in the metabolism of benzene, benzene oxide itself is highly unstable and has not yet been isolated in the metabolism of benzene. Although no metabolites of oxepin were found by Jerina and coworkers (1968), oxepin is known to be in equilibrium with benzene oxide and is thus included in the pathway diagrams. The conversion of benzene oxide to phenol was conclusively shown to be nonenzymatic but catalyzed by acid, protein, simple peptides, or acetamide (Jerina et al., 1968).

The role of benzene oxide in benzene metabolism, while not conclusively demonstrated, is nonetheless generally accepted. In this respect, benzene metabolism seems analagous to the metabolism of various other aromatic hydrocarbons which also involve arene oxide intermediates (Jerina et al., 1970; Kaubisch et al., 1972). In addition, the bone marrow toxicity of benzene might be related to the formation of benzene oxide because the latter is an electrophile with alkylating properties (Daly et al., 1972). General reviews of arene oxide formation have recently appeared supporting the role of benzene oxide in benzene metabolism based on the common metabolites of the two compounds, particularly on the formation of trans-1,2-dihydro-1,2-dihydroxybenzene and the mercapturic acid precursor (Jerina, 1974; Jerina and Daly, 1974).

(3) Kinetics of Benzene Metabolism and Elimination

For the most part, the kinetics of benzene metabolism in mammals has not received detailed attention. Parke and Williams (1953a) administered C^{14}-benzene to rabbits by gastric intubation at doses ranging from 340 mg/kg to 500 mg/kg and attempted to monitor all metabolites over a thirty to seventy hour period. A partial summary of their results is presented in Table XIV.

Table XIV: Metabolic Fate of a Single Dose of ^{14}C-labelled Benzene Administered to Rabbits by Gastric Intubation, 30-70 Hours After Dosing (Parke and Williams, 1953a)

Nature of metabolite	% of dose (average)		
Benzene exhaled unchanged	43	44.5 in expired air	77 (79)#
Respiratory CO_2	1.5		
Phenol*	23.5	32.6 in urine	
Catechol*	2.2		
Quinol*	4.8		
Hydroxyquinol*	0.3		
trans-trans-Muconic acid	1.3		
-Phenylmercapturic acid	0.5		
(Urinary radioactivity)	(34.5)		
Metabolized benzene in tissues and faeces†	About 5-10 in body		
Total accounted for	84-89%		

* These phenols are excreted conjugated
† About 0.5% of dose in faeces
# Benzene in expired air + urinary radioactivity.

Although most of the dose was eliminated by the third day, elimination measured as urinary metabolites dropped precipitously to only 0.3% in the fourth through seventh days after benzene administration. Measurements of ^{14}C-labelled CO_2 were not made after the third day, thus a potential shift in excretory pathways cannot be determined.

Most of the more recent studies on benzene metabolism have been concerned with monitoring urinary phenol or benzene elimination from the lungs. Bakke and Scheline (1970) administered benzene by stomach tube at doses of 100 mg/kg and 1000 mg/kg to rats and found that only 3.1-3.7% was excreted as urinary phenol after 48 hours. This low level of urinary phenol was inconsistent with the

above work of Parke and Williams (1953a) on rabbit as well as the study by Cornish and Ryan (1965), which indicated that rats metabolized 23% of an intraperitoneal dose of benzene (400 mg/kg) to urinary phenolic compounds.

Measurements of unchanged benzene in expired air and urinary phenol have been suggested as techniques for determining levels of occupation exposure to benzene (Sherwood, 1972). In measuring respiratory elimination in man, Sherwood found evidence for a two compartment system of elimination, the first having a half life of 2.5 hours and the second of about 22 hours (see Figure 12).

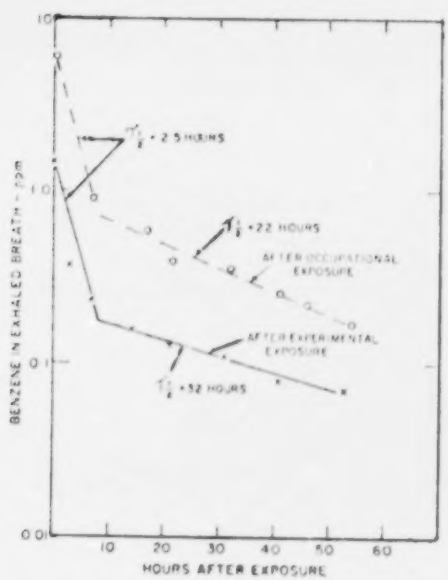


Figure 12: Elimination of Benzene in Exhaled Breath of One Subject After Unspecified Experimental and Occupational Exposure of About 4 hours. (Sherwood, 1972) Courtesy of Pergamon Press Ltd.

This type of elimination pattern is indicative of rapid elimination of benzene from the lungs to the alveolar air with less rapid removal of benzene from the body tissues.

Hunter and Blair (1972) have correlated percent body fat to percent of benzene excreted vs. urinary phenol after exposure to benzene vapor, as illustrated in Table XV.

Table XV: The Factors and Times of Post-Exposure Observations, Benzene Doses and Excretions in 5 Adult Males Exposed to the Vapours of Benzene on Single Occasions (Hunter and Blair, 1972)

Subject number	Body fat (% wt)	Concentration of benzene in test atmosphere (µg/l)	Post-exposure time of observation (hr)	Dose Benzene (mg)	Weight of benzene excreted as phenol (mg)	Excreted benzene as percentage of dose (% wt)
1	8.3	63	24.7	33.0	16.7	50.6
		309	49.8	118.0	70.0	59.4
		133	30.8	184.0	139.3	75.7
2	13.0	340	31.9	116.0	85.0	73.3
3	16.0	328	48.0	117.0	90.7	77.6
4	18.2	328	30.5	75.0	64.4	85.9
		88	38.2	167.0	137.6	82.4
5	19.7	103	28.9	99.0	71.3	72.0
		294	29.5	217.0	170.3	78.5
		405	23.0	58.0	49.1	84.6
		107	43.5	52.0	45.3	87.1

From this, it was postulated that benzene accumulation in the body probably occurs in the fat deposits, although Parke and Williams (1953a) noted only 2.6% of a benzene dose in rabbit fat two days after exposure. In further

contrast to studies in nonhuman mammals, Hunter and Blair (1972) calculated that only 12% of a benzene dose is eliminated unchanged in expired air in man.

(c) Degradation by Plants

Benzene has recently been isolated from pineapple (Flath and Forry, 1970). However, the potential role of plants in the degradation of benzene has not been extensively investigated in the United States. Jansen (1964) found that benzene-^{14}C can be synthesized from ethylene-^{14}C in avocados. In a subsequent study exposing avocados to benzene-^{14}C vapor, 25-28% of the benzene was absorbed by the plant and 0.004-0.007% was metabolized to $^{14}CO_2$. In addition, volatile and nonvolatile substances other than benzene were noted (Jansen and Olson, 1969). Similar results have been recently reported by Durmishidze and coworkers (1974), who reported that potatoes, apples, tomatoes, quince, pepper, lemons, grapefruit, tung, and bananas absorb ^{14}C-benzene from the atmosphere at benzene levels of 10 mg/l. Most of the benzene is converted to muconic, fumaric, succinic acids, and phenylalanine with only a small amount being oxidized to CO_2.

Benzene degradation by plants has received considerable attention in the U.S.S.R. Durmishidze and Ugrekhelidze (1967) found that tea, laurel, grape, and corn roots absorbed radiolabelled benzene, which was subsequently metabolized to CO_2 in all parts of the plants. Tea plants administered ^{14}C-benzene through the roots were

found to convert 16% of the total dose to organic and amino acids. In this experiment, the following metabolic pathway was proposed: Benzene → Phenol → Catechol → o-Benzoquinone → Muconic acid (Durmishidze and Ugrekhelidze, 1969). Grapes, during all stages of growth including germination, are reported to oxidize ^{14}C-benzene to CO_2 and other aliphatic compounds (Tkhelidze, 1969). More recently, peas administered ^{14}C-benzene through the roots have metabolized benzene using copper containing enzymes including o-diphenol oxidase (Ugrekhelidze and Chrikishvili, 1974).

In summary, there is a strong indication that plants may perform a major role in the degradation and synthesis of benzene in the environment.

2. Chemical and Photochemical

The available studies on the photochemical degradation or alteration of benzene under environmental conditions (wavelengths of light >290 nm) have been previously reviewed in Section III. No other chemical reactions, which might take place under environmental conditions, have been noted in the literature.

B. Transport

Transport of benzene from the point of release to various points in the environment is not well understood. In fact, only Pilar and Graydon (1973) have presented convincing evidence that the source of benzene in air in correlated to automotive emissions. However, from the physical properties of benzene some projections of benzene distribution in the environment are

possible. The relatively high water solubility (1780 mg/ℓ at 25°C) and vapor pressure (95.2 mm Hg at 25°C) are perhaps the most important parameters. From these parameters, Mackay and Wolkoff (1973) have calculated that the half-life of benzene, undergoing constant mixing and at less than saturation concentrations in a square meter of water, would be 37 minutes. In comparison, n-octane's half-life would be 3.8 seconds; DDT, 3.7 days; and dieldrin, 723 days. However, because of its fairly high solubility in water, benzene will probably be washed out of the atmosphere with rain and thus a continuous cycling between air and water would occur.

Neely et al. (1974) have demonstrated a relationship between octanol-water partition coefficients and bioconcentration potential in fish. Although the logarithm of the partition coefficient for benzene (2.13) is outside the region treated by Neely et al. (1974), the calculated bioconcentration factor, nineteen, would suggest little potential for bioaccumulation.

In summary, although little is known about the transport of benzene in the environment, based on physical properties the compound should be quite mobile with a low bioaccumulation potential.

VI. EVALUATION

A. Summary

Benzene is a major synthetic organic chemical intermediate which is probably being produced at a rate of about ten billion pounds per year. Over the period from 1963 to 1973, benzene production more than doubled. However, because benzene is derived primarily from petroleum products and the petroleum market is currently in a state of flux, it is difficult to estimate the continued growth potential of benzene. For the most part, production sites are localized in areas rich in raw materials; petroleum based production concentrated along the Texas Gulf and coal based production in the northeast and south central area. Commercial use of benzene is similarly localized but the amount used in the northeast seems considerably more than the amount produced, thus requiring transport of benzene from the Texas Gulf to the northeast.

Benzene is also a significant constituent of gasoline (about 1% by weight) and automotive exhausts ($\sim$ 4%). Unlike the chemical intermediate usage, benzene release from these sources is much more diffuse and probably approximates population density distribution.

Although precise estimates of benzene release are difficult to make, approximate calculations indicate benzene release into the environment approaches 1.8 billion pounds annually. Total motor vehicle emissions make up well over half of this release. Release from commercial use probably does not exceed 30% of the total. Other sources are relatively insignificant: production a little over 2% and oil spills under 1% of total release.

The relatively high volatility and water solubility of benzene would indicate that significant amounts of benzene could reside both in the atmosphere and in aquatic systems. Although no direct studies have been encountered on the bioaccumulation of benzene, benzene's octanol-water partition coefficient does not indicate a high potential for bioaccumulation in fish.

Due to the high degree of resonance stabilization in the unsubstituted aromatic ring, benzene is a relatively stable hydrocarbon. Under environmental conditions, the rates of hydrolysis and oxidation are probably negligible. Although photochemically initiated reactions may be a factor in benzene degradation, these processes also seem to proceed at a relatively slow rate and their significance is difficult to assess with the information currently available.

The biological stability of benzene under environmental conditions is similarly difficult to estimate. A variety of pure cultures of microorganisms have been shown to possess enzymatic systems capable of metabolizing benzene at concentrations much greater than would be expected in the environment. However, with mixed cultures in the standard 5 day BOD test or using Warburg respirometry technique, only a slight increase in the respiration rate was observed. When the microbial respiration rates of benzene are compared to presumably stable analogs of benzene, such as 1,3,5-trichlorobenzene, it seems that while benzene may be susceptible to microbial attack, its rate of degradation by microorganisms would be slow at best. Mammals and plants are also capable of metabolizing benzene, but the ultimate degradation - i.e., breakdown to carbon dioxide and water - is slight. Nevertheless, the alteration of benzene to phenolic conjugates by plants may be a significant environmental process for the removal of benzene.

The available monitoring information supports the experimental data on the chemical and biological behavior of benzene, indicating that benzene is at least moderately persistent and a potential contaminant of both air and water. However, benzene monitoring data is incomplete at best. With the exception of the air monitoring done by Pilar and Grayden (1970), fixed-interval measurements in the same area over extended periods have not been made. Thus, most monitoring studies are of little use in determining the major source(s) of benzene pollution. Similarly, only Novak and coworkers (1973) offer reliable quantitative measurements of benzene water contamination. However, even with these limitations, the monitoring information does suggest that benzene may be a widespread air and water contaminant in the low ppb range. Also, the monitoring data suggest that benzene is partially resistant to normal drinking water treatment procedures. While the work of Pilar and Grayden (1970) indicates automotive exhaust as a major source of benzene air contamination, the relatively high level (23 ppm) found by Smoyer and coworkers (1971) near a solvent reclamation plant suggests that industries handling benzene may also be significant sources of contamination.

B. Recommendations

Given the type of information currently available on the biological degradation of benzene, little can be concluded about benzene's persistence. At the presumably low (ppb) background levels found in the aquatic environment, substrate inhibition would not be expected and benzene degradation may proceed by the pathways previously described. Equally probable, the enzyme(s) required to hydroxylate benzene may not be active at low benzene levels or in the presence of other suitable carbon sources. These possibilities could be easily

examined using ^{14}C-labelled benzene at low (10-100 ppb) concentrations in mixed or pure cultures of microorganisms commonly found in fresh water, salt water, or sewage treatment plants. The effects of temperature and alternate substrates should also be examined. Similarly, the importance of benzene adsorption by vegetation should also be examined in the low ppm range.

While the methods for the quantitative determination of benzene in air seem satisfactory, the only quantitative method used for benzene in water is the inert gas stripping technique of Novak and coworkers (1973). The technique of gas stripping followed by concentration on a gas chromatographic column (EPA, 1974) appears to be a desirable method for determining low concentrations of benzene in water, although no benzene was detected in the water examined (EPA, 1974). The reliability and limits of detection of the techniques probably should be examined further.

More extensive benzene monitoring should be considered a necessity. Besides the obvious need for more extensive air and water analysis, monitoring might be most productively concentrated near benzene production and by-product manufacturing plants in order to quantitate the losses. The 1% loss during benzene production used in this report may well be conservative, especially for coke-based production where considerable loss could take place during stoking of the ovens. The calculated losses (100% minus % yield of final product) during by-product manufacturing are upper limits since the loss is assumed to to be entirely benzene. Much of the actual loss during certain operations may occur between the intermediate and final product stage. Detailed monitoring studies would, no doubt, provide more realistic estimates of benzene loss from manufacture and use.

The relative environmental hazard from benzene contamination requires the integration of information on release to the environment, persistence in the environment, and toxicological considerations. This report has only considered the first two parameters. Final recommendations for further study of benzene contamination must also be based on considerations of possible biological effects of benzene as well as information on other environmental contaminants which may be equally important. Furthermore, it should be noted that if relative losses of benzene projected in this report are confirmed by monitoring data, the possibility for effective remedial action (i.e., elimination of benzene losses from automotive emissions) seems rather remote.

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